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AMERICAN
JOURNAL OF BOTANY

Vol. V NOVEMBER, 1918 No. 9

CALCIUM OXALATE IN THE DASHEEN*

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Calcium oxalate enters into the composition of a great variety of plants. As it is a quite insoluble salt, when synthesized by the plant it separates as a solid from the plant juices. It is probably formed during protein metabolism and is considered by most authorities as a waste product of such action, although a few plant physiologists maintain that it is dissolved and utilized in the further growth of the plant. However, the solid crystals may easily be detected under the microscope in various forms in plant tissues. Not infrequently they are found in bundles of fine, needle-like crystals packed in cells and surrounded by a mucilaginous liquid. Crystals of this character are called "raphides," and the cells containing them when brought in contact with water have the property of ejecting the individual needles which float out slowly into the surrounding medium. Plants which produce calcium oxalate in this form, when eaten raw, invariably cause a painful burning sensation in the mouth, the obvious explanation of which is that when the cells full of needles meet the saliva of the mouth the needles are ejected and penetrate the mucous membrane, although other explanations are conceivable.

Among the plants which synthesize calcium oxalate in this interesting form is the dasheen (*Colocasia esculenta* (L.) Schott.), which has been introduced into this country by the Office of Seed and Plant Introduction of the United States Department of Agriculture, and has been successfully grown in Florida, where it has shown every promise of becoming a valuable addition to our vegetable food supply. The tubers of this plant can be utilized as a substitute for potatoes, while the large leaves when boiled have proved excellent greens. There

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[The **Journal** for October (5: 397–446) was issued Nov. 9, 1918.]

has, nevertheless, been a distinct prejudice against the plant which has acted adversely to its extended use, due to the intensely acrid taste of the raw leaves and to a less degree of the tubers. Both portions of the plant were known to possess the raphide-filled cells, and this has been assumed to be the cause of their acridity. There were, however, certain reasons for suspecting that this was not entirely the case, and as the plant is one of considerable food value it seemed advisable to make a study of it in this respect.

The evidence that raphides are calcium oxalate and not calcium citrate is very complete, although some confusion has existed on this point, as the two salts have many properties in common. By careful analytical work F. G. Kohl[1] has shown beyond reasonable doubt that raphides are the oxalate, and quite recently H. Ziegenspeck,[2] who seems to be unfamiliar with Kohl's research, has prepared from raphides pure oxalic acid which he identified by its characteristic physical properties, thus furnishing absolutely conclusive proof of the composition of the crystals.

On the question of the cause of the acrid taste of raphide-containing plants the evidence is less direct. Much has been written about such plants, the general opinion seeming to be that the raphides serve as a protection to the plants against animals and insects, although one writer, A. Schneider,[3] takes the ground that such is not the case, but, on the contrary, that calcium oxalate crystals serve the plants as a tissue support and add to their structural rigidity. E. Stahl[4] studied the effect of a variety of raphide-bearing plants when fed to hungry snails and reached the conclusion that the burning taste depends on the raphides alone, but his conclusion is arrived at through a process of reasoning rather than by experiment. The experiment of Barnes[5] has a more direct bearing on the question. He macerated a raphide-bearing plant in water and then subjected it to filtration through such a fine filtering medium that no raphides could pass. The resulting filtrate showed no sign of acridity, and hence he concluded that the raphides were solely responsible by mechanically irritating the mouth. As raphides were not the only material removed by the filtration, his conclusion was rather more sweeping than the experiment warranted.

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[1] Anatomisch-physiologische Untersuchungen der Kalksalze und der Kieselsäure in der Pflanze. p. 91. Marburg, 1889.

[2] Ber. Deutsch. Bot. Ges. **32**: 630–633. 1915.

[3] Bot. Gaz. **32**: 142–144. 1901.

[4] Pflanzen und Schnecken. Jena, 1886.

[5] Barnes, C. R. Bot. Gaz. **13**: 232–233. 1888.

Samples of dasheen, both tubers and leaves, were placed at the writer's disposal through the kindness of Mr. R. A. Young, of the Office of Foreign Seed and Plant Introduction, and they were used in the work which follows in an endeavor to settle the point as to whether the raphide content was the sole factor in causing the acridity of this plant.

The family of the Araceae to which the dasheen belongs is known to produce in several instances alkaloids, glucosides, and bitter substances, any of which if present in the plant under investigation might be wholly or partially responsible for its peculiar flavor. Samples of dasheen leaves were, therefore, distilled with steam on the assumption that they might contain a volatile compound, possibly an alkaloid. The distillate, however, failed to show the presence of any body of this nature. Further experiments were made on the dried leaves, which were exhaustively extracted with various solvents, namely, petroleum ether, ethyl ether, chloroform, acetic ether, alcohol, and water in rotation. These extracts, likewise, after evaporating the solvent, showed no evidence of an acrid flavor, but the observation was made that the residual leaf matter was no longer unpleasant to the taste, although when examined under the microscope the raphide cells were still intact and apparently in perfect condition. At first sight this seemed to be proof that the raphides had no connection with the acrid taste of the leaves, but on further investigation it was found that when cells from these extracted leaves were brought into contact with water they had wholly lost their capacity to expel the individual needle crystals, a fact which might very well acount for their loss of virulence. The facts brought out in this series of experiments, namely, that the various extracts and the residue were all without acrid effect, seem to force us back on the raphide theory of acridity, with the additional proviso that free movement of the raphides is necessary to secure the effect. It might, nevertheless, be contended that acridity is destroyed in the process of extraction by the decomposition of some compound, though the possibility seems remote.

To secure more direct evidence of the mechanical effect of raphides on the mouth an attempt was made, with a moderate degree of success, to synthesize calcium oxalate in fine needle forms as near as could be in size and shape to naturally-occurring raphides. It was found that when a dilute solution of calcium chloride was slowly dropped into a dilute solution of oxalic acid, crystals of calcium oxalate separated, which were of sharp monoclinic form and largely admixed with needle-like crystals quite similar to natural raphides and of approximately the same size. To observe the effect of this preparation on the mouth, the crystals were filtered, washed with water, dried, and then incorporated in melted paraffin. When the gum thus produced was masticated for a short while it left in the mouth a burning sensation comparable to that experienced from dasheen leaves, though less intense.

An endeavor to isolate the naturally-formed raphides was only partially successful, but the attempt served to bring out further evidence that the raphides are responsible for the acrid taste. Corms of the Indian turnip (*Arisaema triphyllum* (L.) Torr.) were used in this experiment, since they are easily obtained in the vicinity of Washington, contain raphides in large quantities, and have an intensely acrid flavor. The turnip-like corms were peeled, washed, and grated to a pulp which was supended in distilled water for some time to allow the needle crystals to work out of the cells. The mixture was then filtered by suction through a rather coarse cloth, stirred up again with water and again filtered. A drop of filtrate, under the microscope, showed the presence of many needle crystals mixed with some starch granules. The filtrate was next centrifuged, the supernatant liquid poured off, the residue stirred up with distilled water and again centrifuged, this process being carried through several times until the mixed raphides and starch had been well washed. The solid residue from these operations had an intensely acrid flavor, differing in no respect from that of the untreated tuber.

An endeavor was made to obtain the raphides in a still purer form by eliminating the starch through the action of diastase. The washed mixture of starch and raphides was subjected to the action of yeast over night at a temperature of 40° C. When the preparation was examined the following morning, however, no raphides were found in it, and, moreover, it had lost entirely its acrid taste. This experiment, therefore, while it failed of its original object, nevertheless offers strong additional proof that raphides are the cause of acridity.

In repeating the above described experiment on the dasheen, similar observations were made.

CONCLUSIONS

All experimental evidence goes to show that calcium oxalate crystals are the sole cause of the acrid taste of the dasheen by the mechanical irritation of the mucous membrane of the mouth.

As the acrid flavor can readily be removed by proper methods of cooking,[6] there is no reason why the presence of raphides should interfere with the use of the plant as a vegetable.

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[6] Young, R. A. Yearbook U. S. Dept. Agric. 1916. pp. 203–206.